AD634728

QUARTERLY REPORT NO. 10

CONTRACT NO. DA 19-129-AMC-152(N)(OI9116)

WITH

U. S. ARMY NATICK LABORATORIES

Report Period: 26 November 1965 - 26 February 1966

SYNTHESIS AND POLYMERIZATION OF FLUORINATED SULFUR MODIFIED NITROSO RUBBER

By

Eugene C. Stump, Calvin D. Padgett
and Charles R. Wetzel

26 March 1966

Peninsular ChemResearch, Inc.
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FOREWORD

This report was prepared by Peninsular ChemResearch, Inc., under Contract No. DA 19-129-(AMC)-152(N)(C 116) for the U. S. Army Natick Laboratories with Mr. C. B. Griffis as Project Officer. This is the tenth Quarterly Report under this contract and covers the period 26 November 1965 through 26 February 1966.

Personnel engaged in this research are Eugene C. Stump, Project Supervisor (123 hours), Calvin D. Padgett, Research Chemist (494-1/4 hours), and Charles R. Wetzel, Research Chemist (472-3/4 hours). Analytical work was performed under the supervision of Van A. May. Drs. Paul Tarrant and George Butler are acting consultants.

It is estimated that 85% of the work is completed and that 77.54% of the estimated costs have been incurred to date. To the contractor's best knowledge the funds remaining unexpended are sufficient to complete the work called for in the contract.

ABSTRACT

Tetrafluoroallene has been prepared and terpolymerized with $CF_3NO/CF_2=CF_2$. Additional samples of methyl γ-nitrosoperfluorobutyrate were prepared and polymerized with $CF_3NO/CF_2=CF_2$. Several unsuccessful attempts were made to cross-link terpolymers containing $CF_2=CFBr$, $CF_2=CFCF=CF_2$, C_6F_5NO, $CF_2=C=CF_2$ and $CF_2=CFCH=CH_2$. A low temperature polymerization unit has been installed and is now in operation.

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I. INTRODUCTION

The research described in this report is part of a continuing program sponsored by the U. S. Army Natick Laboratories and concerned with the development of so-called "nitroso rubber," a 1:1 copolymer of trifluoronitrosomethane and tetrafluoroethylene. A list of references describing prior research was given in the First Quarterly Report.

The primary objective of this contract was to enhance the desirable properties, in particular the low-temperature flexibility, of nitroso rubber by the incorporation of sulfur atoms in a modified polymer structure. Secondary objectives included the synthesis of desirable monomers, including monomers not containing sulfur, and their polymerization in the nitroso rubber system. This research has been described in previous reports.

During the course of the contract the objectives were modified and increased in scope. Recent work, and work described in this report, has been directed toward the preparation of nitroso terpolymers containing a reactive site for cross-linking.

II. DISCUSSION

A. Monomer Synthesis

The synthesis of tetrafluoroallene[1, 2, 3] has been reported in the literature and was accomplished during this quarter to provide a new monomer for terpolymerization. This compound is prepared by the following sequence:

$$CF_2Br_2 + CH_2=CF_2 \xrightarrow{Bz_2O_2} CF_2BrCH_2CF_2Br$$

$$CF_2BrCH_2CF_2Br \xrightarrow{KOH} CF_2BrCH=CF_2 + CF_2=C=CF_2$$

$$CF_2BrCH=CF_2 \xrightarrow{KOH} CF_2=C=CF_2$$

Literature yields for the last reaction are low, ranging from 11 to 34% depending upon conditions. Small amounts of the allene are also obtained in the initial dehydrobromination (1-5%). The average conversion to tetrafluoroallene (from the propene) in our laboratories was 10%. The initial dehydrobromination gave 6% $CF_2=C=CF_2$. Best results were obtained by adding $CF_2BrCH=CF_2$ to KOH pellets at 80° with stirring, while passing a slow stream of nitrogen through the system. No volatile products were obtained when powdered KOH was used. An infrared spectrum of tetrafluoroallene is shown in Figure 2.

Additional samples of methyl γ-nitrosoperfluorobutyrate were prepared. It has been found that decarboxylation of the nitrite can be effected by ultraviolet irradiation as well as by pyrolysis to give similar conversions.

(1) T. J. Jacobs and R. S. Bauer, J. Am. Chem. Soc., 81, 606 (1959).

(2) T. J. Jacobs and R. S. Bauer, U. S. Patent 3, 148, 223 (8 Sept. 1964).

(3) Banks, Haszeldine and Taylor, J. Chem. Soc., 985 (1965).

$$ONOOC(CF_2)_3CO_2CH_3 \xrightarrow[\Delta]{vac.} ON(CF_2)_3CO_2CH_3\ (19\text{-}22\%) + CO_2$$

$$ONOOC(CF_2)_3CO_2CH_3 \xrightarrow[u.v.]{vac.} ON(CF_2)_3CO_2CH_3 (20\%) + CO_2$$

Pyrolysis of the nitrite ester gives a higher boiling, clear fraction in addition to the blue nitroso ester. This material is believed to be a diester resulting from radical combination as shown.

$$2\ ONOOC(CF_2)_3CO_2CH_3 \xrightarrow[\Delta]{} 2CH_3O_2C(CF_2)_3\cdot + 2CO_2 + 2NO$$

$$\downarrow$$

$$CH_3O_2C(CF_2)_6CO_2CH_3$$

The higher boiling material is formed in about the same conversion (21-24%) as the nitroso ester. An infrared spectrum, Figure 3, shows typical ester absorption as well as C-H absorption. Pyrolysis at higher temperatures (350°-400°) results in the formation of a high-boiling purple liquid, possibly a nitroxide[4]. Photolysis of the nitrite ester gives, in addition to higher boilers, by-products which apparently contain a nitro group.

The photolytic decomposition is the preferred method of preparation since it requires less attention and regulation.

An attempt has been made to prepare an unsaturated nitroso compound by reaction of methyl nitrite with perfluorobutadiene. Although no reaction was apparent in the absence of light, exposure to sunlight produced a light blue-green liquid, which rapidly lost its color during attempted purification. An infrared spectrum of this material (Figure 4) shows C-H absorption as well as peaks which might be attributed to C=C, $-NO_2$ and -ONO groups. The desired reaction is shown below.

$$CH_3ONO + CF_2{=}CFCF{=}CF_2 \longrightarrow CH_3OCF_2CF{=}CFCF_2NO$$

$$\text{and/or } CH_3OCF_2\underset{\underset{NO}{\mid}}{C}FCF{=}CF_2$$

(4) W. D. Blackley, J. Am. Chem. Soc., 88, 480 (1966).

B. Polymerization

In addition to nitroso ester terpolymers and other previously reported terpolymers, a new terpolymer containing tetrafluoroallene was prepared during this report period (Table 1). Polymers ranging from an oil to a gum have been obtained, with conversions of 50-85%. Tetrafluoroallene could enter the growing chain ether by a head-to-head or head-to-tail mechanism to give a pendent $=CF_2$ group. The possibility that tetrafluoroallene might also react with tetrafluoro-

$$CF_3NO + CF_2{=}CF_2 + CF_2{=}C{=}CF_2 \longrightarrow -\underset{\displaystyle CF_3}{\underset{|}{N}}OCF_2\underset{\displaystyle CF_2}{\underset{\|}{C}}\!-\!\!-\!\underset{\displaystyle CF_3}{\underset{|}{N}}O- \text{ and/or } -\underset{\displaystyle CF_3}{\underset{|}{N}}OCF_2\underset{\displaystyle CF_2}{\underset{\|}{C}}\!-\!O\underset{\displaystyle CF_3}{\underset{|}{N}}-$$

ethylene as well as CF_3NO can not be ruled out at this time. An infrared spectrum of the terpolymer (Figure 5) exhibits a strong peak at 5.68 microns, probably due to $>C=CF_2$ absorption. The remainder of the spectrum is similar to that of $CF_3NO/CF_2=CF_2$ except for several shifts in absorption frequency.

Construction and installation of a low temperature polymerization system utilizing a 2-l. Parr No. 4501 pressure reactor has been completed. The low-temperature polymerization apparatus (shown in Figure 1) consists of five components. The compressor (A) cools a reservoir (B) of $CaCl_2$ solution which is circulated by a pump (C) through a polymerization bath (D) and an autoclave (E).

(A) The compressor is a commercial unit, a 1.5 horse-power Copelametic, which uses R-502 as a refrigerant. The compressor is connected to two large copper coils sealed inside the reservoir.

(B) The reservoir is a tank 12" x 18" x 36" containing two cooling coils from the compressor bathed in the coolant which is circulated throughout the system. Near the bottom the reservoir has an outlet tube which leads to the pump and at the top an inlet tube for the return of coolant. The reservoir is filled with 20 gal. of a 29.6% $CaCl_2$ solution which is gravity fed to the pump and can be maintained at any temperature between ambient and -40° within 1.5°F. It is insulated on all sides with six inches of polystyrene and encased in a vapor sealed plywood box.

(C) The first pump used in the system was an Oberdorfer centrifugal pump connected directly to a 3450 RPM motor, but it was found that this unit was transferring too much heat to the cooling system. The situation was remedied by adapting an ordinary pump used for circulating water in lab-scale distillations, a 1/30 horse-power PK pump. This pump was connected to the system through 5/8" copper tubing and then insulated with polyurethane foam. The pump is gravity fed from the reservoir and forces the coolant through the polymerization bath and autoclave and then through the return inlet at the top of the reservoir.

(D) The polymerization bath is a steel tank 12" x 18" x 18" surrounded by a water jacket 9" high and 1-1/2" wide. The $CaCl_2$ solution from the reservoir is circulated through the jacket which is baffled so that the coolant must circulate completely around the tank which is filled with $CHCl_3$ to a depth of six inches. Three inches from the top of the tank a 3/4" brass rod mounted in air-tight bearings at each wall extends the length of the tank and six inches beyond one end. This extended end of the shaft is connected by a rocker arm to pin and bushing mounted off-center in a pully powered by a 1/18 horse-power Bodine motor. the motor is controlled by a Variac to give the degree of agitation desired on the brass rod. Several wire baskets which hold the polymerization vessels are suspended from the brass rod into the $CHCl_3$ bath. The entire tank is insulated with three inches of polyurethane and encased in a wooden box with a removeable, insulated lid.

(E) The autoclave used is a 2000-ml., Parr Series 4500, stirred, pressure reaction vessel with an internal cooling coil. As received from the factory, the cooling coil was made of 1/4" O.D. stainless steel, but after the first run it was apparent that this coil was too small to provide sufficient cooling. It was therefore replaced first with a 1/4"

O. D. copper coil which also proved unsatisfactory and finally a 3/8" O. D. stainless steel coil was used. The autoclave, stirring motor, and holder are encased in a plywood box insulated with five inches of polystyrene and a temperature of -30° C is easily obtained.

One of the major difficulties with the autoclave has been concerned with leaks at low temperatures. It appears that after stirring for an extended length of time at low temperatures leaks develop around the stirring shaft. This shaft is sealed with Rulon cones compressed with a packing nut and it has been found to maintain a pressure of 750 psi at room temperature for several days, but when the temperature was lowered to -30° leaks developed. The autoclave will be fitted with a recently-developed stirring gland (Parr) in hope of eliminating leakage.

The temperature on the autoclave is monitored with a Rustrak automatic chart temperature recorder, Model 144.

C. Cross-Linking

Several attempts have been made to obtain evidence of cross-linking in terpolymers containing $CF_2=CFBr$, $CF_2=CFCF=CF_2$, C_6F_5NO, $CF_2=C=CF_2$ and $CF_2=CFCH=CH_2$ as the termonomer.

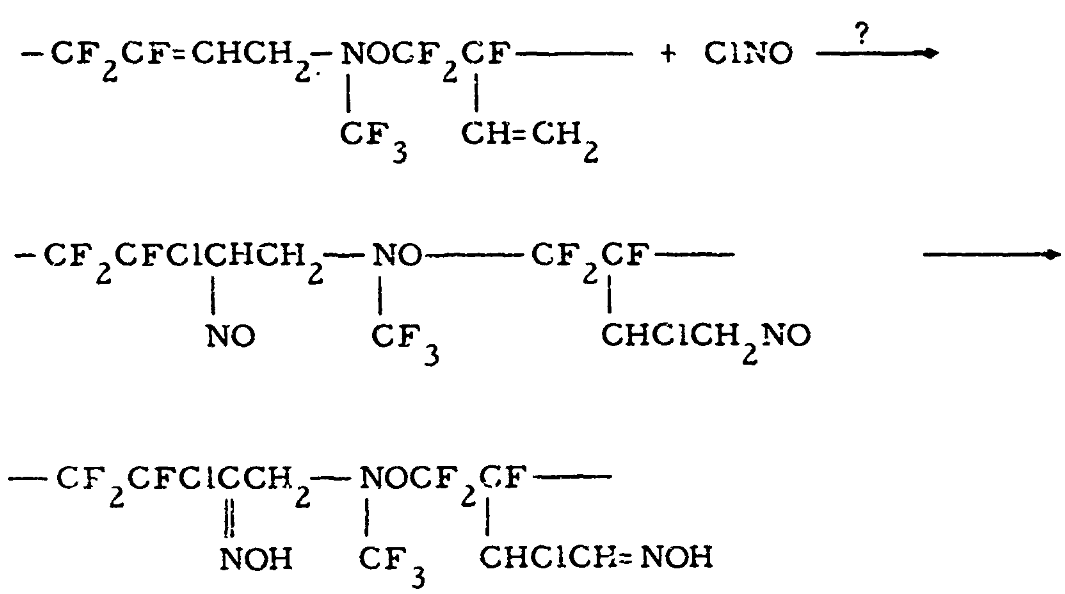
The terpolymer containing $CF_2=CFBr$ was heated in solution with benzoyl peroxide and $(CF_2=CFCH_2CF_2)_2$ in an attempt to obtain addition of the bromine atom across the double bond but no insoluble gel, indicating cross-linking, was obtained.

Nitrosyl chloride was added to the terpolymer containing perfluorobutadiene using the procedure reported previously[5]. The blue polymer containing pendent nitroso groups was then dissolved in Freon 113 and sealed in a Pyrex tube with $CF_2=CF_2$. No gel formation was observed.

(5) Quarterly Report No. 7, this contract, p. 16.

Both the terpolymer containing C_6F_5NO and the terpolymer containing $CF_2=C=CF_2$ were mixed with $NaOCH_2(CF_2)_3CH_2OH$ and heated. In the former case it was felt that a cure might be effected by a nucleophilic displacement of the para fluorine atom on the pentafluorophenyl group. The proposed cure of the $CF_2=C=CF_2$ terpolymer involved addition of the diol across the pendent double bond and/or fluoride replacement to give a $=CFOCH_2(CF_2)_3CH_2O-$ cross-link. No evidence of cross-linking was observed in either case.

The addition of nitrosyl chloride to the terpolymer containing 1, 1, 2-trifluorobutadiene has not been previously reported. This reaction resulted in a colorless gum rather than a blue polymer as with perfluorobutadiene. An infrared spectrum of the polymer showed no double bond absorption indicating nearly complete addition of nitrosyl chloride. Reaction of the polymer in Freon 113 solution with hexafluoroglutaryl chloride gave a cloudy, white suspension. This reaction will be investigated further since it is possible that oxime groups are formed by nitrosyl chloride addition, as shown. These groups might provide a reactive cross-linking site.



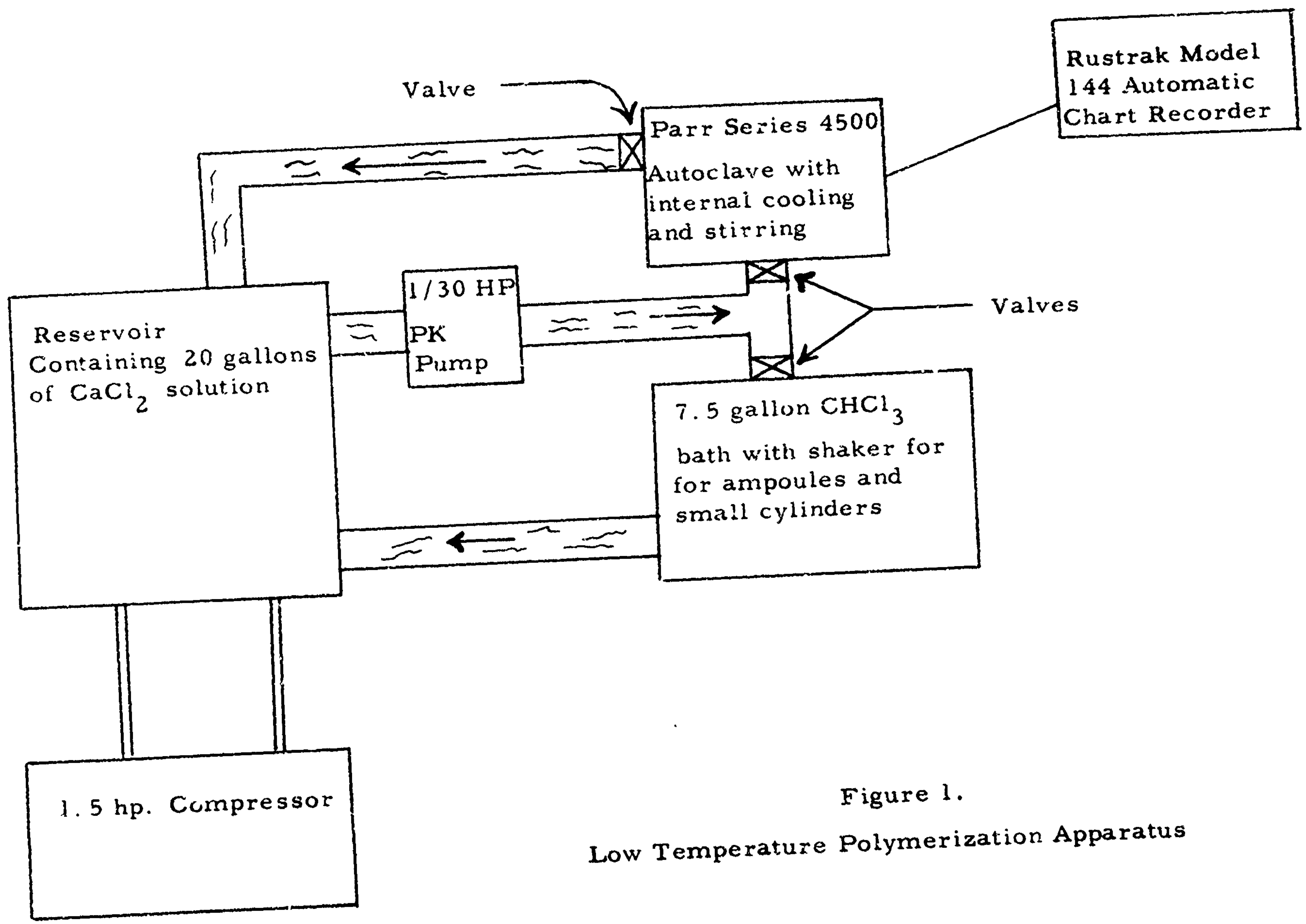


Figure 1.

Low Temperature Polymerization Apparatus

TABLE 1.

Terpolymers

No.	Monomers	Amount Grams	Amount Moles	System	Time Hours	Temp. °C	Yield Grams	Conversion %	Remarks
1.	CF_3NO	2.5	0.025	Bulk	69	-32	2.6	50	Low m. wt. oil.
	$CF_2=CF_2$	1.25	0.0125						
	$CF_2=C=CF_2$	1.40	0.0125						
2.	CF_3NO	4.0	0.040	Bulk	69	-30	4.9	59	Gum; fractionated; $[\eta] = 0.13$; T_g -35°
	$CF_2=CF_2$	2.0	0.020						
	$CF_2=C=CF_2$	2.24	0.020						
3.	CF_3NO	2.0	0.020	Bulk	24	-30	3.5	85	Gum
	$CF_2=CF_2$	1.0	0.010						
	$CF_2=C=CF_2$	1.12	0.010						
4.	CF_3NO	2.0	0.020	Bulk	12	-30 to 25	2.1	50	Viscous liquid.
	$CF_2=CF_2$	1.0	0.010						
	$CF_2=C=CF_2$	1.12	0.010						
5.	CF_3NO	2.88	0.030	Solution in Freon 113	48	-30	10.0	84	Gum; fractionated twice; $[\eta] = 0.16$
	$CF_2=CF_2$	5.0	0.050						
	C_6F_5NO	3.96	0.020						
6.	CF_3NO	3.0	0.030	Bulk	72	-35	—	—	Copolymer, no ester incorporated.
	$CF_2=CF_2$	2.7	0.027						
	p-$CF_2=CF_2C_6H_4CO_2C_2H_5$	0.7	0.003						

TABLE 1. (Continued)

Terpolymers

No.	Monomers	Amount Grams	Amount Moles	System	Time Hours	Temp. °C	Yield Grams	Conversion %	Remarks
7.	CF_3NO	1.8	0.018	Bulk	72	ambient	0	0	Starting material recovered.
	$CCl_2=CClCCl=CCl_2$	4.6	0.018						
8.	CF_3NO	4.0	0.040	Bulk	48	-35	6.1	66	Sticky gum, $[\eta] = 0.15$
	$CF_2=CF_2$	2.0	0.020						
	$CF_2=CFCF=CF_2$	3.2	0.020						
9.	CF_3NO	18.9	0.191	Bulk	24	-32	22.5	50	$[\eta] = 0.26$
	$CF_2=CF_2$	21.2	0.212						
	$ON(CF_2)_3CO_2CH_3$	5.5	0.021						
10.	CF_3NO	16.7	0.169	Bulk	24	-32	21.0	44	$[\eta] = 0.29$
	$CF_2=CF_2$	21.2	0.212						
	$ON(CF_2)_3CO_2CH_3$	10.1	0.042						
11.	CF_3NO	21.1	0.213	Suspension	96	-35	42	69	Shaker broke after several hours, brown gum.
	$CF_2=CF_2$	26.9	0.269						
	$ON(CF_2)_3CO_2CH_3$	12.5	0.052						

III. EXPERIMENTAL

A. Monomer Synthesis

1. Tetrafluoroallene

a. $CF_2BrCH_2CF_2Br$ [6]

Five similar preparations were carried out in a 1.4 l. autoclave. Another preparation on a larger scale was carried out in a 3 l. autoclave. The following is a description of a series of three preparations.

Dibromodifluoromethane (4.5 mole), 1,1-difluoroethylene (1.0 moles) and benzoyl peroxide (10.0 g.) was heated in a 1.4 l. stainless-steel rocking autoclave at 110° for five hours. CF_2Br_2 and $CF_2{=}CH_2$ were recovered by low-temperature distillation leaving a residue containing the product, $CF_2BrCH_2CF_2Br$, and telomers of $CF_2Br(CH_2CF_2)_nBr$. After 2 additional runs utilizing recovered material, combination and distillation of the residue gave 270 g. of $CF_2BrCH_2CF_2Br$ (b.p. 72-75°/300 mm) from a total of 132 g. of $CH_2{=}CF_2$ consumed (49.5% yield).

b. $CF_2BrCH{=}CF_2$ [6]

Four preparations were carried out, the most successful being similar to a recent literature method[7].

1,3-Dibromo-1,1,3,3-tetrafluoropropane (90 g. 0.33 moles) was added drop-wise to potassium hydroxide pellets (200 g.) in a 500-ml. flask fitted with a stainless-steel chain stirrer driven by a high torque motor. A nitrogen pressure of 300 to 350 mm. was maintained in the system with a slow sweep into traps at -78 and -196°. The flask was heated to 60°. As dehydrobromination occurred the reaction mixture became dark and sticky.

(6) P. Tarrant, A. Lovelace and M. Lilyquist, J. Am. Chem. Soc., 77, 2783 (1955).

(7) Banks, Haszeldine and Taylor, J. Chem. Soc., 985 (1965).

Stirring became less efficient and the temperature rose to $\sim$100°. Distillation of the contents of the cold traps gave 6% tetrafluoroallene (2.3 g., 0.02 moles) and 45% 3-bromo-1, 1, 3, 3-tetrafluoropropene (30 g., 0.15 moles). The latter was further distilled through a small glass helix-packed column (b. p. 34°).

c. $\underline{CF_2=C=CF_2}$

Six reactions were carried out using a variety of different conditions. The results were poor. In some cases only a trace of product was obtained and identified by I. R. Analysis. When powdered 90% potassium hydroxide was used at 100° the mixture became molten and no volatile products could be trapped. The following is a description of a more successful reaction.

In a 300-ml. flask fitted with an addition funnel, stainless steel chain stirrer driven by a high torque motor and connected to two traps at -183° was placed 150 g. of pelleted potassium hydroxide. The flask was heated to 80° by a water bath while a slow stream of dry nitrogen was passed through the system. 3-Bromo-1, 1, 3, 3-tetrafluoropropene (30 g., 0.15 moles) was added drop-wise. The low boiling product in the first trap was separated by a vaporization distillation and then purified by distillation on a low temperature still. Tetrafluoroallene (1.8 g., 0.15 moles) was obtained in 10% conversion (b. p. -38°). An infrared spectrum showed adsorption at 4.86, 8.0 and 9.68 microns.

2. <u>1, 1, 2-Trifluorobutadiene</u>

A 1-l., 3-neck flask was fitted with a stirrer, reflux condenser vented to a trap at -78°, and an addition funnel containing $CF_2BrCFClCH=CH_2$ (280 g., 1.26 mole). A mixture of isopropyl alcohol (500 ml.) and activated Zn (130 g.) was stirred at reflux as the olefin was dripped into the flask. The product caught in the -78° trap was vaporized through a $CaCl_2$ tube and further purified by trap to trap distillation. The final product, $CF_2=CF-CH=CH_2$, weighed 124 g. (92% conversion).

3. Methyl γ-Nitrosoperfluorobutyrate

a. $ONOOC(CF_2)_3CO_2CH_3$

This synthesis was carried out six times as previously described.[8] Each run produced about 54g of product for an average conversion of 87%.

b. $ON(CF_2)_3CO_2CH_3$

The nitroso ester was prepared several times. The reaction described below is typical. An addition funnel was placed atop a packed column (Raschig rings) with a 17" heated zone. The column was vented into a 500ml., 3-neck flask which was connected in turn to a vacuum system through a trap cooled to -195°. A vacuum of ~ 0.1 mm. Hg was maintained throughout the system as the freshly prepared nitrite was dropped into the column which was heated to 250°. As the pyrolysis proceded, a light amber liquid collected in the flask while the blue product was collected in the -195° trap. The blue product was washed with water, dried over anhydrous $CaSO_4$, and fractionated on a small packed column to give $CH_3O\text{-}C(=O)\text{-}CF_2CF_2CF_2NO$ b.p. 24-26°/26 mm. The amber liquid product was worked up in a similar manner to give a colorless liquid, b.p. 137-140°/0.10mm. Yields, based on runs using 50g. (0.225 moles) perfluoroglutaric anhydride, were 19-22% of the fractionated $CH_3O\text{-}C(=O)\text{-}CF_2CF_2CF_2NO$ and 21 to 24% of the high boiling liquid with a proposed structure of $(CF_3CF_2CF_2C(=O)\text{-}OCH_3)_2$. A similar reaction at a pyrolysis temperature of 350-400° gave a lower yield of nitroso product and several grams of a purple liquid exhibiting an infrared absorption characteristic of an ester.

Decarboxylation of $CH_3O_2C(CF_2)_3COONO$ could also be effected by u.v. light. Nitrite (40g.) was placed in 1 l. flask (equipped with an immersion well and No. 8A36 Hanovia lamp) which was connected to a vacuum system through a -195° trap. Irradiation was continued for 48 hrs. while a

8. Quarterly Report No. 8, this contract, p. 6.

0.1 mm. pressure was maintained. Combining the blue product of a similar reaction using 33 g. of nitrite gave 12 g. fractionated $CH_3O\text{-}\overset{O}{C}\text{-}CF_2CF_2CF_2NO$ (20%). Another product having a green color was indicated by infrared analysis to be a nitro compound.

4. Reaction of Methyl Nitrite with Perfluorobutadiene

a. Methyl nitrite (1.2g., 20 mmoles) and perfluorobutadiene (1.6 g., 10 mmoles) were charged to a 20-ml. ampoule. No reaction was apparent at room temperature in the absence of light. The ampoule was placed in sunlight for a total of 16 hrs. A [illegible] green liquid resulted. After the unreacted material was removed, an infrared spectrum of the product indicated the reaction product was an unsaturated nitro compound.

b. Methyl nitrite (1.2 g., 20 mmoles) and perfluorobutadiene (1.6 g., 10 mmoles) were charged to a 1-liter flask and irradiated with U. V. light from a Hanovia lamp type 8A36 for 4 hours. A light greenish blue liquid was formed. Concentration of the blue liquid by trap to trap distillation gave only a trace of product, but the color quickly faded. The infrared spectrum was similar to the product obtained above.

B. Polymerization

Polymers prepared during this period are described in Table 1. Procedures for preparing and working up the terpolymers are the same as previously reported.

During this report period, the Parr No. 4501 pressure reactor was connected to the refrigeration system and tested. Although pressures of 750 psig could be maintained for several days at room temperature, it was found that leaks occurred at -30°. Three $CF_3NO/CF_2{=}CF_2$ copolymer runs were attempted with low yields being obtained in each case due to leakage. In a typical polymerization the reactor was charged with water (1000 g.), LiBr (530 g.) and $MgCO_3$(35 g.) and cooled to the desired temperature. Trifluoronitrosomethane (99g., 1.0 mole) and tetrafluoroethylene (100 g., 1.0 mole) were charged to the reactor by volatilization from small cylinders. The pressure rose to a maximum of 200 psig. but dropped to 0 psig. within 24 hrs. The solution was acidified and the coagulant removed and dissolved in Freon 113. The polymer was precipitated by methanol and dried under vacuum.

C. Cross-Linking

1. $\underline{CF_3NO/CF_2=CF_2/CF_2=CFBr}$ Terpolymer

Four grams of a $CF_3NO/C_2F_4/C_2F_3Br$ terpolymer was dissolved in 20 ml. of FC-43 and the solution refluxed with 1 ml. of $(CF_2=CFCH_2CF_2-)_2$ and 2 g. of benzoyl peroxide. No insoluble material separated as would be expected had cross-linking occurred.

The experiment was repeated using divinyltetramethyldisiloxane with the same results.

2. $\underline{CF_3NO/CF_2=CF_2/CF_2=CFCF=CF_2}$ Nitrosyl Chloride Reacted Terpolymer

Two grams of a terpolymer of $CF_3NO/C_2F_4/C_4F_6$ was dissolved in Freon 113, and the solution was placed in a sealed tube with excess ClNO. After 2 days the overgases were removed and a pale blue polymer was precipitated by addition of CH_3OH. A solution of 0.6 g. of this polymer in several ml. of Freon 113 was placed in a sealed tube with 11 mmole of C_2F_4. The tube was placed in a -30° bath for several days and then allowed to warm to room temperature. After several weeks there was still no apparent indication of cross-linking.

3. $CF_3NO/CF_2=CF_2/C_6F_5NO$ Terpolymer

An 8 g. sample of $CF_3NO(3)/CF_2=CF_2(5)/C_6F_5NO(2)$ terpolymer was thoroughly mixed with 5 wt. % $NaOCH_2(CF_2)_3CH_2OH$ on a small rubber mill.[9] Curing was attempted by pressing samples between aluminum foil sheets at 150° and 220° for 1/2, 1 and 2 hrs. without evidence of cross-linking Oven heating at 100° for 24 hrs. produced no change.

4. $CF_3NO/CF_2=CF_2/CF_2=C=CF_2$ Terpolymer

a. A 3.5 g. sample of $CF_3NO(2)/CF_2=CF(1)/CF_2=C=CF_2(1)$ was thoroughly mixed with 5 wt. % $NaOCH_2(CF_2)_3CH_2OH$ on a small rubber mill. Attempted cure as above gave no evidence of cross-linking.

b. Terpolymer (0.2 g.) was dissolved in 4 ml. of Freon 113 and charged to a 13 ml. ampoule with CF_3NO(1 g., 10 mmoles). The ampoule was allowed to stand at room temperature for 6 days with no apparent reaction. Infrared spectrum of the reprecipitated polymer was identical with the unreacted polymer.

5. $CF_3NO/CF_2=CF_2/CF_2=CFCH=CH_2$ Nitrosyl Chloride Reacted Polymer

An 80-ml. Fischer-Porter tube was charged with three grams $CF_3NO/C_2F_4/CF_2=CFCH=CH_2$ terpolymer dissolved in 10 ml. of $CF_2ClCFCl_2$. The tube was frozen, evacuated, and ClNO (2.5 g., 39 mmole) was condensed in. When the tube warmed to room temperature a dark red solution resulted. The material was pumped to dryness under vacuum and the residue was dissolved in Freon 113. A gum was precipitated by addition of CH_3OH and it was dried in a vacuum desiccator. An infrared spectrum of this material showed no double bond absorption. A small amount of the product was dissolved in Freon 113 and a drop of perfluoroglutaryl chloride was added to produce a cloudy, white suspension.

(9) Through the cooperation of Dr. H. C. Brown, Department of Chemistry, University of Florida, Gainesville, Florida.

D. Synthesis of Intermediates

1. Perfluoroglutaric Anhydride

Perfluoroglutaric anhydride was prepared as previously reported[8] in conversions of 81 and 77%. A total of 1068 g. was prepared.

2. Perfluorosuccinic Anhydride

Perfluorosuccinic acid (200 g., 1.05 moles) was mixed with excess P_2O_5 in a 1-l. flask. The mixture was heated and perfluorosuccinic anhydride (141 g., 0.82 mole) was removed by distillation as formed.

3. Methyl Nitrite

Methyl nitrite was prepared as previously reported[10] by reaction of methanol, sodium nitrite and sulfuric acid. The product (126 g.) was obtained in 70% conversion.

4. Mon odium 2, 2, 3, 3, 4, 4-Hexafluoropentanediol

Hexafluoropentanediol (21.2 g. 0.10 mole) and sodium (1.15 g. 0.05 mole) in 200 ml. of dry ether were stirred by means of an air motor for 48 hours. Formation of a white solid occurred slowly. After filtering and drying under vacuum for six hours 12 g. of $NaOCH_2CF_2CF_2CF_2CH_2OH$ was collected. Evaporation of ether solution yielded 9 g. of the unreacted diol.

(10) Quarterly Report No. 8, this contract. p. 13.

TABLE 2

$CF_3NO/CF_2=CF_2$ Suspension Polymerization

No.	Monomer	Amount Grams	Amount Moles	Time Hours	Temp. °C	Yield Grams	Conversion %	Remarks
1.	CF_3NO	99	1.0	24	-15	10	5	Cooling coil fractured, allowing monomer to escape.
	$CF_2=CF_2$	100	1.0					
2.	CF_3NO	50.1	.51	48	-30	10	10	No monomer recovered; reactor apparently leaked.
	$CF_2=CF_2$	51	.51					
3.	CF_3NO	50.4	.51	48	-30	30	30	10 g. monomer recovered.
	$CF_2=CF_2$	50.5	.51					

IV. MONOMER PROCUREMENT

During this report period the following sample was received from outside sources:

$CF_2=CFCF_2CFClCF_2CF=CF_2$	29 g.	University of Colorado

V. SAMPLES SUBMITTED

During this report period the following samples were submitted to the U. S. Army Natick Laboratories for evaluation:

Designation	Charged Composition	Amount
QC-58.1	$CF_3NO(9)/CF_2{=}CF_2(10)/ON(CF_2)_3CO_2CH_3(1)$	22.5 g.
QC-59.1	$CF_3NO(4)/CF_2{=}CF_2(5)/ON(CF_2)_3CO_2CH_3(1)$	16.4 g.

VI. MONOMER LIST

The monomers described below have been added to the list given in previous reports.

Number	Monomer
427	$CF_2=C=CF_2$
428	$CCl_2=CCl-CCl=CCl_2$

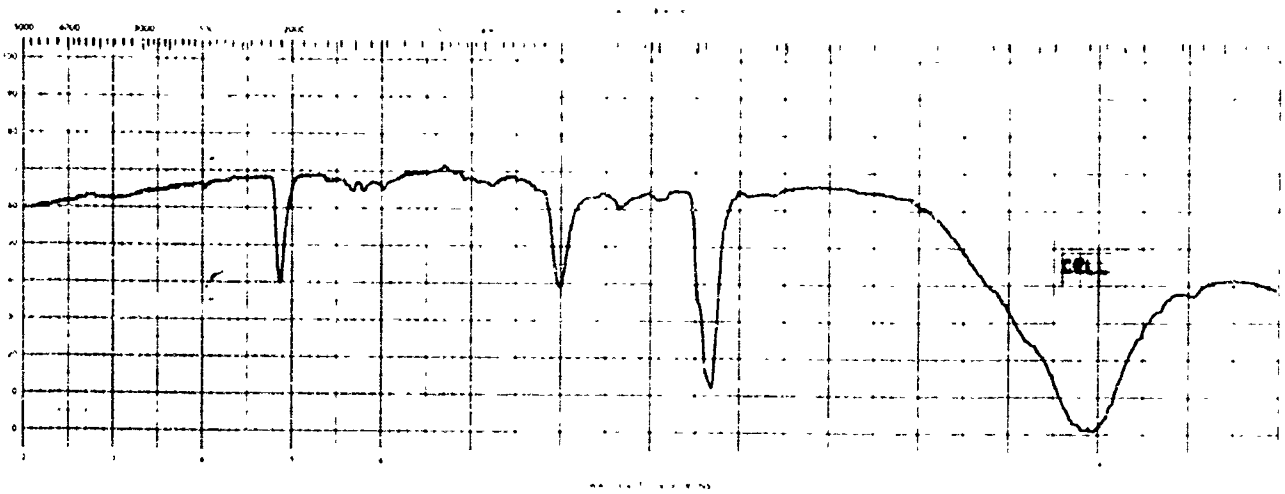


Figure 2. Infrared Spectrum of $CF_2=C=CF_2$

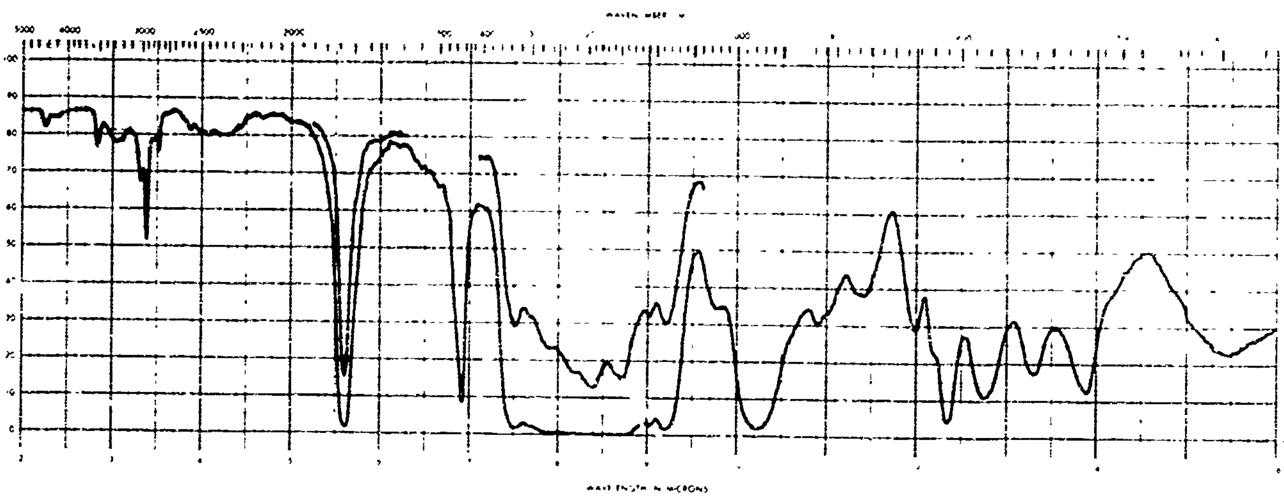


Figure 3. Infrared Spectrum of High-Boiling Product from $ONOOC(CF_2)_3CO_2CH_3$ Pyrolysis

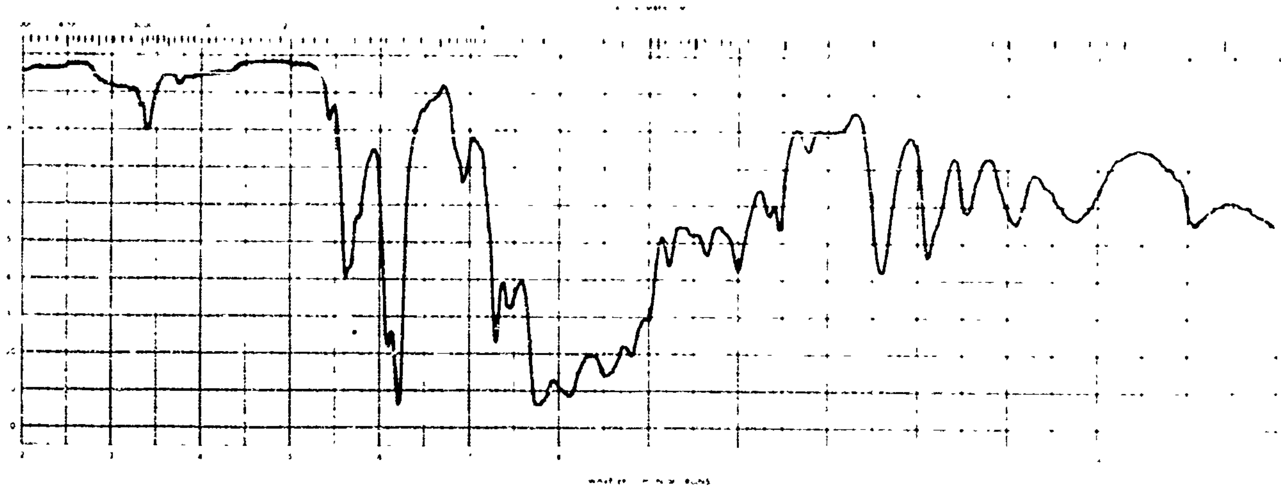


Figure 4. Infrared Spectrum of Product from $CH_3ONO/CF_2=CFCF=CF_2$ Reaction

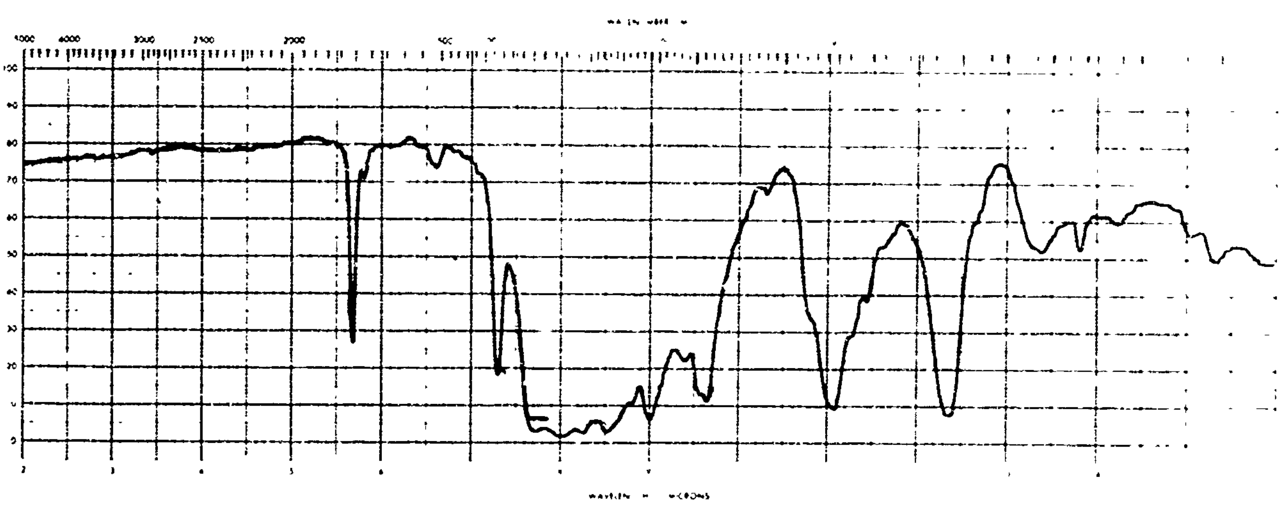


Figure 5. Infrared Spectrum of $CF_3NO(2)/CF_2=CF_2(1)/CF_2=C=CF_2(1)$ Terpolymer

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1. ORIGINATING ACTIVITY (Corporate author)

Peninsular ChemResearch, Inc.
Gainesville
Florida 32601

3. REPORT TITLE

SYNTHESIS AND POLYMERIZATION OF FLUORINATED SULFUR MODIFIED NITROSO RUBBER

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Quarterly Report 26 November 1965 - 26 February 1966

5. AUTHOR(S) (Last name, first name, initial)

Stump, Eugene C., Padgett, Calvin D., and Wetzel, Charles R.

6. REPORT DATE 26 March 1966	7a. TOTAL NO. OF PAGES 23	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO. DA 19-129-AMC-152(N)(019116)	9a. ORIGINATOR'S REPORT NUMBER(S) 10	
b. PROJECT NO.		
d	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) 66-32 CM	

10. AVAILABILITY/LIMITATION NOTICES

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U.S. Army Natick Laboratories Natick, Mass. 01760 Clothing and Organic Materials Division

13. ABSTRACT

Tetrafluoroallene has been prepared and terpolymerized with $CF_3NO/CF_2{=}CF_2$. Additional samples of methyl γ-nitrosoperfluorobutyrate were prepared and polymerized with $CF_3NO/CF_2{=}CF_2$. Several unsuccessful attempts were made to cross-link terpolymers containing $CF_2{=}CFBr$, $CF_2{=}CFCF{=}CF_2$, C_6F_5NO, $CF_2{=}C{=}CF_2$ and $CF_2{=}CFCH{=}CH_2$. A low temperature polymerization unit has been installed and is now in operation.

DD FORM 1 JAN 64 1473

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Polymerization	9					
Fluorochemicals	1					
Sulfur	1					
[illegible]	4					

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